

学校编码: 10384

密级_____

学号: 22620091151213

厦门大学

硕 士 学 位 论 文

闽南沿海大气 PM_{10} 中有机酸的分布与来源 研究

Study on sources and distributions of organic acids in PM_{10}
in the coastal regions of southern Fujian

刘碧莲

指导教师姓名: 吴水平 副教授

专 业 名 称: 环 境 科 学

论文提交日期: 2012 年 5 月

论文答辩时间: 2012 年 6 月

2012 年 6 月

厦门大学博硕士论文摘要库

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为王新红课题组的研究成果,获得实验室的资助,所有相关实验均在本实验室完成。

声明人(签名):

2012年6月 日

厦门大学博硕士论文摘要库

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（ ☒ ） 1. 经厦门大学保密委员会审查核定的保密学位论文
于 年 月 日解密，解密后适用上述授权。

（ ☒ ） 2. 不保密，适用上述授权。

声明人（签名）：

2012 年 6 月 日

厦门大学博硕士论文摘要库

目 录

摘要	VI
Abstract.....	VIII
第 1 章 前言.....	1
1.1 研究背景及目的.....	1
1.2 研究内容和技术路线.....	2
第 2 章 研究进展	4
2.1 有机酸物理化学性质.....	4
2.2 有机酸分析方法.....	7
2.2.1 气相色谱/质谱联用 (GC/MS)	7
2.2.2 毛细管电泳 (CE)	8
2.2.3 离子色谱法 (IC)	9
2.2.4 高效液相色谱 (HPLC)	9
2.3 大气颗粒物中有机酸污染水平和变化特征研究.....	10
2.3.1 有机酸污染水平研究.....	10
2.3.2 有机酸季节及昼夜变化特征研究.....	10
2.4 气/粒分配研究	11
2.5 有机酸来源分析.....	12
2.6 有机酸的环境效应和健康影响.....	13
第 3 章 实验部分	15
3.1 闽南沿海大气 PM ₁₀ 样品采集	15
3.1.1 研究区域介绍.....	15
3.1.2 采样点设置.....	16
3.1.3 采样时间及采样器.....	18
3.2 有机酸一次源谱样品采集.....	19
3.3 样品处理与保存.....	21
3.4 样品分析.....	22

3.4.1 样品预处理.....	22
3.4.2 样品定性和定量分析.....	22
3.5 质量控制与质量保证.....	24
第 4 章 闽南沿海大气 PM ₁₀ 中有机酸的污染特征分析.....	27
4.1 闽南沿海大气 PM ₁₀ 变化特征分析	27
4.1.1 闽南沿海大气 PM ₁₀ 季节及空间变化特征	27
4.1.2 闽南沿海大气 PM ₁₀ 昼夜变化特征	28
4.2 闽南沿海大气 PM ₁₀ 中有机酸的组成	29
4.3 闽南沿海大气 PM ₁₀ 中有机酸季节变化特征	37
4.3.1 闽南沿海大气 PM ₁₀ 中有机酸总浓度季节变化	37
4.3.2 闽南沿海大气 PM ₁₀ 中有机酸各组分浓度季节变化	40
4.3.3 闽南沿海大气 PM ₁₀ 中有机酸污染水平	44
4.4 闽南沿海大气 PM ₁₀ 中有机酸昼夜变化特征	47
4.5 闽南沿海大气 PM ₁₀ 有机酸空间分布特征	52
第 5 章 大气 PM ₁₀ 中有机酸源谱特征及来源分析	55
5.1 大气 PM ₁₀ 中有机酸源谱特征分析	55
5.2 大气 PM ₁₀ 中有机酸来源分析	56
5.2.1 部分有机酸相关性分析.....	56
5.2.2 特征比值分析.....	61
5.2.3 多元统计分析.....	66
第 6 章 结论与展望.....	71
参考文献.....	73
附录	83
致谢	84

Contents

Abstract in Chinese	VI
Abstract	VIII
Chapter 1 Introduction	1
1.1 Research backgrounds and purposes	1
1.2 Contents and research route	2
Chapter 2 Overview	4
2.1 Physicochemical properties of organic acids	4
2.2 Analytical methods of organic acids	4
2.2.1 GC/MS	7
2.2.2 CE	7
2.2.3 IC	8
2.2.4 HPLC	9
2.3 The levels and distributions of organic acids in atmosphere	10
2.3.1 The levels of organic acids	10
2.3.2 The seasonal and diurnal variations of organic acids	10
2.4 The gas/particle distributions of organic acids in atmosphere	11
2.5 The sources of organic acids in atmosphere	12
2.6 The environmental and health effects of organic acids in atmosphere	13
Chapter 3 Materials and methods	15
3.1 Samples of PM ₁₀ in the coastal regions of southern Fujian	15
3.1.1 Research region	15
3.1.2 Sampling sites	16
3.1.3 Sampling time and sampler	18
3.2 Samples of source spectrum	19
3.3 Pretreatment and storage of samples	21
3.4 Analysis of samples	22
3.4.1 Preprocessing of samples	22

3.4.2 Qualitative and quantitative analysis of samples	22
3.5 QA and QC	24
Chapter 4 Pollution characteristics of organic acids in PM₁₀ in the coastal regions of southern Fujian	27
4.1 Characteristics of PM₁₀ in the coastal regions of southern Fujian.....	27
4.1.1 Seasonal and spatial variations of PM ₁₀ in the coastal regions of southern Fujian.....	27
4.1.2 Diurnal variations of PM ₁₀ in the coastal regions of southern Fujian...	28
4.2 Compositions of organic acids in PM₁₀ in the coastal regions of southern Fujian	29
4.3 Seasonal variation characteristics of organic acids in PM₁₀ in the coastal regions of southern Fujian	37
4.3.1 Seasonal variations of total concentration of organic acids in PM ₁₀ in the coastal regions of southern Fujian	37
4.3.2 Seasonal variations of individual components concentration of organic acids in PM ₁₀ in the coastal regions of southern Fujian.....	40
4.3.3 Pollution levels of organic acids in PM ₁₀ in the coastal regions of southern Fujian.....	44
4.4 Diurnal variation characteristics of organic acids in PM₁₀ in the coastal regions of southern Fujian	47
4.5 Spatial variation characteristics of organic acids in PM₁₀ in the coastal regions of southern Fujian	52
Chapter 5 The characteristics of source spectrum and the sources of organic acids in PM₁₀.....	55
5.1 The relative spectrum distributions of organic acids of source samples..	55
5.2 The sources of organic acids in PM₁₀	56
5.2.1 Correlation analysis of part organic acids.....	56
5.2.2 Characteristic ratio analysis	61

5.2.2 Multivariate statistical analysis	66
Chapter 6 Conclusions and prospections	71
References	73
Appendix	83
Acknowledgements	84

厦门大学博硕士论文摘要库

摘要

有机酸是大气气溶胶中重要的一类极性有机化合物，来源于机动车尾气、化石燃料和生物质燃烧及烹饪油烟等，不饱和脂肪酸和芳香烃（如苯、甲苯、萘）的光化学氧化以及高等植物及微生物等也有贡献。大气气溶胶中有机酸对全球的气候环境（如辐射平衡、降雨）和人类健康具有重要的影响。闽南沿海（此文定义包括厦门、金门、漳州和泉州部分沿海区域）是中国沿海经济较为发达的区域之一，也是海峡西岸经济区建设的主要引擎之一。近年来随着大厦门城市化和经济的快速发展，空气质量呈现逐年下降的趋势（首要污染物为可吸入颗粒物 PM_{10} ），而有机酸是 PM_{10} 中受人类活动影响明显的重要有机组成之一，有必要对其时空分布和来源进行研究。

在闽南沿海设置 10 个大气 PM_{10} 采样点，于 2010 年 4 月至 2011 年 3 月分月采集昼夜样品（3 次/月），并对样品中 15 种有机酸进行定性和定量分析，分别对其组成特征、季节变化特征、昼夜变化特征及空间变异特征等进行讨论，并结合可能的排放源，对机动车尾气、烹饪油烟、生物质燃烧、土壤及路面尘等进行有机酸源谱特征分析，以期对闽南沿海 PM_{10} 中有机酸的来源进行定性和定量分析，进一步探讨人类活动对空气质量的影响。通过以上研究，得到以下结果：

1、闽南沿海大气 PM_{10} 中有机酸以乙二酸（di- C_2 ）浓度为最高，其次为十六烷酸（ $C_{16:0}$ ），十八烷酸（ $C_{18:0}$ ）或丙二酸（di- C_3 ），其中夏季邻苯二甲酸（Ph）的浓度要高于 $C_{18:0}$ ；受季风和排放源的影响，有机酸总浓度季节变化表现为春冬高夏秋低，而 di- C_3 和 Ph 表现为夏季高，区别于其它有机酸春冬高的特点。

2、不同季节有机酸总浓度普遍表现为昼高夜低，但差异并不显著，说明存在光化学转化的影响；厦门地区一元酸均呈现昼高夜低趋势，但二元羧酸中的壬二酸表现为昼低夜高的特征，其余二元羧酸大部分表现为昼高夜低的特征；金门地区一元酸和二元酸均表现为昼高夜低的特征。

3、受本地排放源强度的影响，有机酸总浓度在厦门和泉州站点高于金门站点，其中金门烈屿国中为金门地区浓度最高点，厦大海洋楼和晋江安海成功小学两采样点浓度居高；与其它地区报道的结果相比，闽南沿海大气 PM_{10} 中有机酸总浓度污染水平较低，仅高于海洋和偏远地区，而二元羧酸的含量远低于中国内

陆城市。

4、源谱分析显示, $C_{16:0}$ 和 $C_{18:0}$ 可指示土壤和地面尘, $di-C_9$ 可指示木材燃烧, $C_{16:0}$ 可指示生物质燃烧, Ph 可指示机动车尾气, 亚油酸 ($C_{18:2}$) 和油酸 ($C_{18:1}$) 可指示烹饪油烟; 来源特征比值 ($di-C_3/di-C_4$ 、 $di-C_6/di-C_9$ 和 $Ph/di-C_9$) 及多元统计分析 (PCA 和多元线性回归) 分析显示, 闽南沿海大气 PM_{10} 中有机酸来自机动车尾气和烹饪油烟占 29.13 % 以上, 而春季受耕种和外来尘输入的影响显示土壤/路面尘的贡献达 21.24 %, 夏季光化学转化输入贡献达 21.01 %; 不同季节未知源类的贡献约占一半, 表明大气 PM_{10} 中有机酸来源较为复杂。

关键词: 有机酸; 季节变化; 昼夜变化; 源谱分布; 污染来源

Abstract

Organic acids are an important kind of polar organic compounds in the atmospheric aerosols. The organic acids in atmospheric aerosols may result from direct emissions (like vehicle exhaust, combustion processes of fossil and biomass, cooking) and secondary photochemical reactions (like oxidative degradation of unsaturated fatty acids and aromatic hydrocarbons). In addition, biogenic sources of organic acids including higher plants and microorganisms emissions also contribute to the compounds in PM_{10} . They have been extensively studied mainly because they play an important potential role in affecting the global climate and human health. they may have direct and indirect effects on the earth's radiation balance by scattering incoming solar radiation, and increase the acidity of rainfall. The Great Xiamen Bay (including Xiamen, Kinmen, part of Zhangzhou and Quanzhou) is an important engine of Western Taiwan Straits Economic Zone. With the rapid development of urbanization and economy, large amount of air pollutants emitted due to energy consumption have deteriorated the atmospheric environment (PM_{10} as the primary air pollutant). Thus, it is important to investigate the temporal and spatial variations and source contributions of organic acids in PM_{10} due to the anthropogenic activity in the coastal regions of southern Fujian.

In this study, the PM_{10} samples were collected on quartz filters with high-volume air samplers in the coastal regions of southern Fujian. The sampling sites include Xiamen (two sites), Quanzhou (three sites) and Kinmen (five sites). The PM_{10} samples were collected three times a month from April 2010 to February 2011, conducted daytime and nighttime every time. Fifteen kinds of organic acids were detected for PM_{10} samples, including saturated and unsaturated monocarboxylic acids ($C_{16:0}$, $C_{18:0}$, $C_{18:2}$, $C_{18:1}$ and $t-C_{18:1}$), dicarboxylic acids in the range of $di-C_2 \sim di-C_{10}$ and aromatic acids (Ph). The characteristics of compositions, seasonal variations, diurnal variations, spatial variations and so on have been discussed. The simulated source samples, including vehicle exhaust, cooking fumes, biomass burning, soil and road dust, have been collected and analyzed. So as to analyze the sources of organic

acid in PM₁₀ in the coastal regions of southern Fujian by applying both qualitative and quantitative methods, and further discuss the influence of human activities to the air quality. Depending on all above studies, we can obtain the results as follows:

1. Oxalic acid (di-C₂) was found as the most abundant species in PM₁₀ in the coastal regions of southern Fujian, followed by palmitic acid (C_{16:0}), stearic acid (C_{18:0}) or malonic acid (di-C₃), but the abundance of phthalic acid (Ph) was higher than C_{18:0} in summer. The seasonal variations were influenced by monsoon and emission sources, the concentrations of total organic acids were higher in winter and spring than that in summer and autumn. The concentrations of monocarboxylic acids, dicarboxylic acids were also higher in winter and spring, except for some species like di-C₃ and Ph.

2. The concentrations of total organic acids were generally higher during the day in four seasons, indicating that most organic acids were photochemical products. In comparison with di-C₉, the concentrations of monocarboxylic acids and most carboxylic acids tended to be high in the daytime and low at night in Xiamen area. The trends of diurnal variations of monocarboxylic and carboxylic acids were more consistent in Kinmen area, which showed the concentrations were higher during the day.

3. Spatial variations of organic diacids were characterized by higher concentrations in the Xiamen and Quanzhou area and lower concentrations in the Kinmen area, and the highest concentrations were observed in the traffic, residential, industrial or mixed area during winter and spring. However the pollution levels of organic acids in PM₁₀ in the coastal regions of southern Fujian were generally lower.

4. The analytical results of source spectrum indicated that soil and road dust, wood burning, biomass burning, vehicle exhaust and cooking fumes were characterized by C_{16:0} and C_{18:0}, di-C₉, C_{16:0}, Ph, C_{18:2} and C_{18:1} respectively. Utilizing those source spectrums analytical results, based on the ratios of malonate acid to succinate acid (di-C₃/di-C₄), which were used to distinguish primary sources from secondary sources of diacids, it could be found that secondary sources contribute more than primary ones in the summer. The ratios of adipic acid to azelaic acid and phthalic acid to azelaic

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库